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Characterizing the Ignition behavior of n-heptane and iso-octane by Eigenvalue Analysis of a Detailed Reaction Mechanism

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Abstract

A numerical analysis of the stabilization process of exothermal reactions in the low temperature oxidation scheme is presented. A perfectly stirred reactor is modeled by using a detailed combustion reaction mechanism for n-heptane and iso-octane oxidation. A continuation method combined with a bifurcation analysis is applied to determine the steady states in the low temperature oxidation regime. The analysis of the steady states for a given parameter set shows, that the detailed mechanism is able to represent the two expected singularities in the low temperature oxidation regime which correspond to the first stage and second stage ignition. Furthermore a branch of steady states is found which represents stabilized cool flames. Three characteristic singularities are found on this branch, indicating the stability limits of steady states of cool flames. Oscillatory events may result in critical states which lead to extinction or to multi step ignition events.

Keywords: Cool Flames, Low temperature oxidation

1. Introduction

Premixing of fuel and oxidizer has been identified as a key technology in combustion engineering to improve combustion efficiency and reduction of emission of pollutants. On the one hand for gaseous fuels premixing is state of the art in many applications, on the other hand the implementation of premixing technology for liquid fuels still reveals some significant challenges. The temperatures needed for complete evaporation of (technical) fuels with a significant content of alkanes like diesel and IGO are associated with the boiling range with boiling temperatures typically between $100°C$ and $350°C$. Problematic for technical systems is that the diesel auto ignition temperature of approximately $220°C$ is far below the upper limit of the boiling range. This is exemplary shown in Fig. 1(a) for diesel and some other fuels. Hence premixing of diesel and air is a critical process since temperatures above auto ignition temperature are needed and the risk of auto ignition is given. It has been shown, that the premixing process for diesel fuel can be stabilized at temperatures above auto ignition temperature without ignition to occur [1]. This can be achieved by making use of the well known NTC behavior (NTC: Negative Temperature-Coefficient) which is a typical phenomena of low temperature alkane oxidation. The role of the NTC behavior for the ignition process is illustrated in Fig. 1(b). It illustrates the ignition behaviour of an alkane-oxidizer mixture fed into a perfectly stirred reactor with a characteristic residence time τ_{res}. For alkanes with more than three carbon atoms ignition may proceed in two steps depending on the boundary conditions. Upon exceeding a characteristic temperature level, which is known as the auto ignition temperature of the fuel τ_I, ignition is initiated by the low temperature oxidation chemistry leading to so called cool flames. These reactions represent the first stage of the two stage ignition process, resulting in rapid fuel and oxygen consumption and rising reactor temperatures. The rapid temperature change due to the first stage ignition is followed by a time interval τ_{II} where the exothermicity of the reaction decreases significantly for increasing reactor temperatures. This
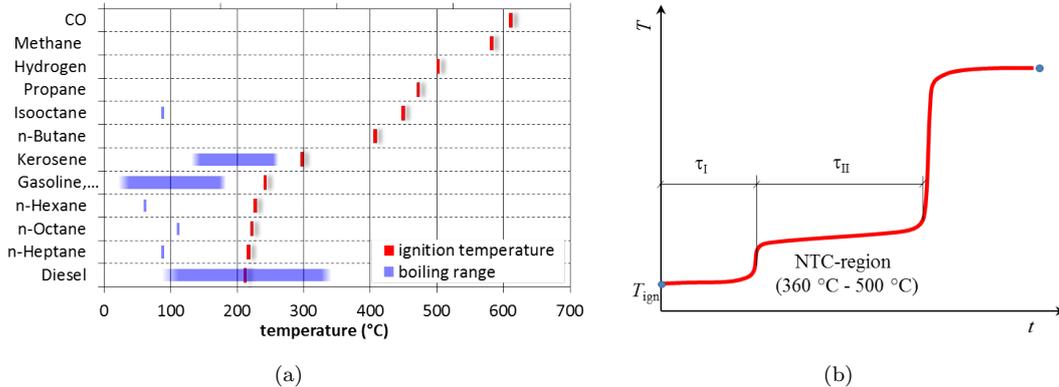
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Figure 1: Auto igntion temperatures and vaporisation range of various fuels (left). Schematic representation of a temperature curve of tow stage ignition of alkanes (right).

phenomenon is known as the negative temperature coefficient of the reaction system. Exceeding again a critical temperature in the reactor the ignition proceeds towards a second stage ignition leading to complete consumption of fuel or oxidizer. The time scales of the complete ignition process $\tau_{\mathrm{ign}} = \tau_{\mathrm{I}} + \tau_{\mathrm{II}}$ are strongly depending on the reactor pressure and the thermal boundary conditions. This can vary by several orders, 10^{-3} to 10^{1} seconds for high pressure combustion at engine conditions and fuel mixing processes at atmospheric pressures, respectively. It has been shown that, at certain boundary conditions, the ignition process can be interrupted after the first stage of ignition which leads to a state of 'stabilized cool flames' at temperatures < 800 K. These moderate temperatures and heat release rates in the NTC-region can be used to support the evaporation process of liquid fuels.

Stabilizing cool flames in technical reactors needs proper control of the boundary conditions. The most important control parameters are the heat loss rate via the reactor walls, the inlet temperature of the reactants and the residence time. To support the control of the process, it is important to know, which modes of reaction instabilities may occur. Whereas second stage ignition and extinction of cool flames can obviously identified as stability limits, other phenomena like oscillatory cool flames are observed. In order to get a deeper insight into the ignition behavior in the low temperature oxidation regime the goal of this paper is to analyze a stoichiometric hydrocarbon-air mixture at temperatures above the ignition temperature. The results are discussed by applying a continuation method, bifurcation analysis and steady state analysis of a detailed combustion reaction mechanism.

2. Approach

In this paper a parametric steady state analysis (PSSA) of an idealized reactor model (PSFR: perfectly stirred flow reactor) is described. A detailed mechanism for n-heptane oxidation is used to investigate the steady states in the low temperature oxidation regime [2, 3]. A requirement for modeling stabilized cool flames is that the system needs to be able to model steady states in the region of low temperature oxidation 500 K $< T < 900$ K:

$$\frac{d\phi}{dt} = 0 \quad \text{with} \quad \phi = f\left(c_i, T, \lambda\right), \tag{1}$$

with c_i the concentration of species i, T temperature and λ representing a parameter which is varied. In our case this will be the inlet temperature T_o of the PSFR. Additionally these steady states need to be (mathematically) stable. The stability of the system is investigated by performing an eigenvalue analysis of the Jacobian Matrix of the system, leading to a set of eigenvalues of the form:

$$e_i = \mathrm{Re}\left(e_i\right) + \mathrm{Im}\left(e_i\right) \tag{2}$$
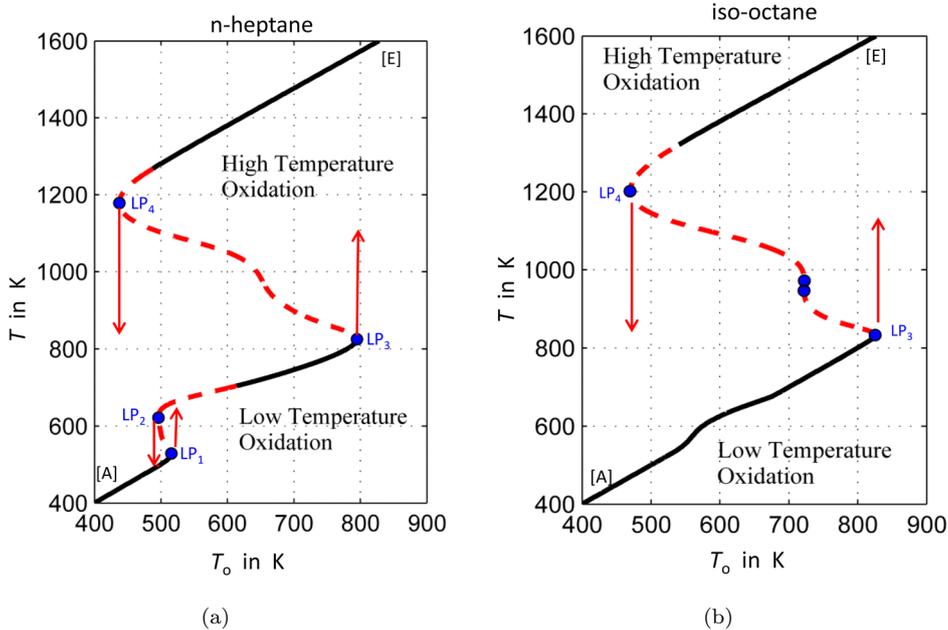
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Figure 2: Steady state locus of a stoichiometric fuel-air mixture in the $T - T_o$ parameter space. Residence time $\tau_{res} = 1$ s and a newtonian cooling time $\tau_N = 0.37$ s. The presented fuels are n-heptane (left) and iso-octane (right).

Those steady state solutions where the Jacobian has real positive eigenvalues, represent unstable solutions, i.e. in case of a small perturbation of a system parameter (e.g. inlet temperature T_o) the deviation will grow in time. Negative real parts represent stable steady states, i.e. at sufficiently small perturbations the deviation from the steady state will decrease with time and the transient solution relaxes to the steady state solution. Non-zero imaginary parts represent oscillatory system behavior, i.e. upon a sufficiently small perturbation the solution oscillates around a steady state solution. A software package for numerical continuation [4] is used to find the steady states of the reacting system when performing the continuation and bifurcation analysis. The result of the applied analysis are solutions for stable and unstable steady states of a non linear systems of equations. Furthermore the points of the solution, where the stability mode of the steady states changes (i.e. singularities if the Jacobian), are determined. They indicate critical points of the solution, e.g. ignition or extinction.

Numerical continuation for large systems of equation is computationally expensive. Especially the numerical evaluation of the Jacobian of the system, which has to be solved several times during each step, leads to relatively long computational times. For this reason, the complete set of equations of the PSFR model and its Jacobian has been provided in symbolic form by using a symbolic math software [5]. Providing the Jacobian of the system in symbolic form reduced calculation times significantly.

3. Results

A PSFR of a stoichiometric fuel-air mixture at atmospheric pressures is modeled with an residence time $\tau_{res} = 1$ s and a newtonian cooling time $\tau_N = 0.37$ s. The applied fuels are n-heptane and iso-octane. The inlet temperature T_o of the reactor is slowly increased by the continuation method. At every temperature T_o the system and it' Jacobian is being analyzed with respect to the steady states and singularities. In Fig. 2(a) and Fig. 2(b) the steady states of a stoichiometric n-heptane-air mixture and a stoichiometric iso-octane-air mixture of a PSFR are shown in the parameter space of reactor temperature T and reactor inlet temperature

T_o. Solid lines represent stable steady states, whereas dashed lines represent unstable steady states. The results of the analysis in Fig. 2(a) show, that for n-heptane the steady state locus has two singularities in the low temperature oxidation regime (LP1; LP2) which represent first stage ignition and extinction of cool flames. The singularities (LP3; LP4) represent the second stage ignition and extinction of the reaction in the high temperature oxidation regime, respectively. The branch between the singularities (LP1; LP2) represents the NTC behavior of the reaction. Stable steady states are associated with stabilized cool flames, whereas unstable steady states represent oscillatory cool flames. For iso-octane shown in Fig. 2(b) no singularities do occur in the low temperature oxidation regime. However, a change in gradient of the locus indicates that some exothermal reactions do occur between 550 K and 750 K. The singularities (LP1; LP2) in the high temperature oxidation regime are indicating, that second stage ignition does occur at similar temperatures for both iso-octane and n-heptane. Remarkably is the difference in the unstable part of the high temperature branch (E; LP2) between both fuels. For n-heptane this unstable part starts at LP4 (roughly 440 K) up to around 460 K, whereas for iso-octane this unstable part starts at LP2 which is slightly higher a temperature (roughly 460 K) compared to n-heptane and ends around 550 K.

4. Conclusions

The results of the analysis performed in this paper give a sound mathematical interpretation of the well known differences in ignition behavior of the hydrocarbons iso-octane and n-heptane. This is strongly related to the exothermal reactions in the low temperature reaction scheme for higher alkanes. This effect results in a first ignition stage at relatively low temperatures, around 500 K, for n-heptane. This first stage ignition is absent for iso-octane oxidation since the low temperature chemistry is less pronounced in this regime. From a technical point of view the presented method gives insight in the temperature regime where cool flames can be stabilized in system. Additionally the results can also be applied to interpret effects like engine knocking which are direct related to unstable cool flames and which should be avoided in engines at all times.

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